

David Taylor Research Center

Bethesda, MD 20084-5000

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DTRC-SME-91/31 June 1991

Ship Materials Engineering Department
Research and Development Report

Influences of Expanding Monomer on Carbon Fiber Reinforced Epoxy Composites II

by
Barbara Howell

Influences of Expanding Monomer on Carbon Fiber
Reinforced Epoxy Composites II

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Abstract

In this investigation it was confirmed that copolymerization of dinorbornene spiroorthocarbonate (DNSOC) with epoxy can eliminate sample shrinkage and even produce sample expansion. To maximize control of shrinkage, it is important to bring epoxy to the gel stage before the DNSOC begins to copolymerize.

DGEBA epoxy was cured with m-phenylenediamine (mPDA) and DNSOC-epoxy samples were cured with mPDA and BF_3 .diethylenetriamine (BF_3 was used to catalyze polymerization of the DNSOC). As compared with carbon fiber reinforced epoxy, the sample with 5% DNSOC showed 33% reduction in interfacial shear stress as measured by the nanoindentation test, and reduction in residual stress perpendicular to the plies by interferometry. However, the significant differences in fiber volume fraction between the epoxy samples can account for some of this apparent reduction. The resin itself showed increases in both tensile strength and tensile modulus when 5% DNSOC was incorporated, and the sample showed no shrinkage.

Administrative information

This report was prepared as part of the Submarine and Surface Materials Block (ND2B) under the sponsorship of Mr. Marlin A. Kinna (ONT 225) and Mr. Ivan L. Caplan (DTRC 0115). Work was performed at this Center under Program Element 62234N, Task No. ND2B, Work Unit 1-2802-950.



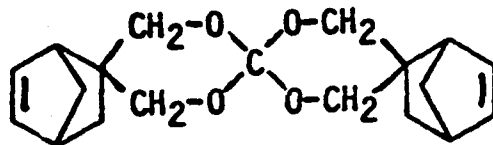
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INTRODUCTION

The concept of copolymerizing an expanding monomer with another polymer, such as epoxy, as a means for controlling shrinkage during polymerization, was conceived by Dr. William Bailey of the University of Maryland (Bailey, 1977). Dr. Bailey has also stated that DNSOC incorporation enhanced mechanical properties (Bailey, 1987).

Tests to measure the usefulness of this concept for a carbon fiber reinforced epoxy composite were performed at the laboratory of Dr. Michael Piggott of the University of Toronto (Lim, 1984). He reported that expanding monomer incorporation increased impact resistance by reduction of residual stress caused by matrix shrinkage, and improved resistance of the composite to moisture degradation. Work at DTRC was designed to verify that inclusion of expanding monomer controls matrix shrinkage and does indeed reduce residual strain.

The expanding monomer chosen for investigation was dinorbornene spiroorthocarbonate (DNSOC), a bicyclic compound which has norbornene groups at the ends.



DNSOC

The norbornene end group has the special function of providing rigidity to the copolymer with epoxy and serves to prevent the reduction in T_g which had been found (Bailey, 1990) for other expanding monomeric compounds which lack this rigidity. Also, DNSOC is appropriate for use with epoxy which reacts by a cationic mechanism. For DNSOC to work effectively, two curing agents are necessary; epoxy is cured with an amine and the DNSOC ring opening is catalyzed by BF_3 .

During FY89, our effort was directed toward: a) finding a reaction mixture which provided good control over epoxy shrinkage, b) establishing proper cure conditions, and c) finding a composition which was transparent enough to allow performance of an embedded single filament tensile test (Howell, 1990). Epoxy mixtures containing 11.7% of DNSOC were used to perform the embedded single filament tensile test, and the fiber fragments were much longer (approx 1 cm) in specimens with DNSOC than in those without it (approx 1 mm). The longer fiber fragments in the DNSOC - containing sample indicate a reduction in interfacial

shear stress and that the matrix was no longer firmly gripping the fibers. On this basis it was concluded that 11.7% of the monomer was much more than was optimal for mechanical property enhancement.

During FY90 carbon fiber reinforced epoxy composites were made on a prepregger, with and without expanding monomer, and curing was done by vacuum bagging in an autoclave.

EXPERIMENTAL

MATERIALS

All reagents were used without further purification.

Epoxy

Epon 815 (Shell Chemical Co.), diglycidyl ether of bisphenol A containing the reactive diluents N-butylglycidyl ether and epichlorohydrin.

DNSOC

Obtained from Epolin, Inc., Newark, N.J.

Curing agents

m-Phenylenediamine (mPDA), (Fluka, AG, Switzerland, 99% purity).

Diethylenetriamine (DETA), (Fluka, AG, Switzerland, 97% purity).

DNSOC catalyst

Boron trifluoride - ethyl etherate (Fluka, AG, Switzerland, 48% BF₃).

Carbon fibers

Hercules (Hercules Aerospace, Magna, UT), AS-4, G size, 12K tow.

METHODS

DNSOC was dispersed into the Epon 815 or Epon 813 epoxy by mixing DNSOC and epoxy in the ratio 25 parts by weight DNSOC to 75 parts by weight epoxy and ballmilling for a week or more. After ball milling, particle size of the DNSOC was measured with a Hegman gauge or determined with a measurement reticle in a light microscope. When ballmilling had been done long enough, particles were 10 micrometers or smaller. It was necessary to use a low viscosity epoxy (approximately 900cp) in order to produce the dispersion.

Shrinkage or expansion was calculated from measured densities. Initial density was obtained by weighing a pipet, drawing up the curing agents mixed with epoxy or epoxy-DNSOC, and reading the volume. When the mixtures had solidified, the

pipets were reweighed. Densities were calculated from these weight and volume measurements. Density after curing was obtained by weighing the samples in air and then in water. Loss of mass in water provided measurement of sample volume, which allowed calculation of density when used with the mass in air. Details of this procedure are specified in ASTM D 792-86.

Boron trifluoride was complexed with diethylene triamine prior to mixing with the other components of epoxy mixtures. To do this, equimolar amounts, measured volumetrically, of boron trifluoride-diethyletherate and diethylenetriamine (DETA) were combined inside a dry box by adding each substance to a 20 mL vial which was then capped.

Shrinkage or expansion was calculated from measured densities (Howell, 1990).

Boron trifluoride was complexed with diethylene triamine (Howell, 1990) prior to mixing with the other components of epoxy mixtures.

PREPARATION OF THE REACTING MIXTURES.

Composition of epoxy control

200 g Epon 815 epoxy
2.1 g DETA
10.86 g mPDA

Composition of DNSOC-epoxy (5 wt% DNSOC)

158 g Epon 815 epoxy
42 g Epon 815 - DNSOC
2.1 g DETA.BF₃
10.86 g mPDA.

DETA and mPDA, or mPDA and DETA.BF₃ were melted together at 70°C, and then mixed into the hot epoxy. Preimpregnated fiber tows (prepreg) using AS-4 carbon fiber were made by Dr. Thomas Juska of the Polymer Composites and Resins Branch, DTRC. on a drum-type prepregger. The epoxy mixture was heated during the prepregging operation to reduce its viscosity and promote fiber wetting. The prepreg was cut into desired sizes, layers were stacked, and the prepreg stacks were cured and consolidated by vacuum bagging in an autoclave at 100°C for four hours and 150°C for 24 hours.

Fiber volume fractions were found by measuring the densities of the matrix materials and that of the composite samples by ASTM method D-792-86. The measurements were made on five samples of each type. In accordance with this procedure, composite samples were digested in nitric acid overnight, and the fibers were collected on preweighed, fritted glass filters. From

these, fiber mass was obtained and subtracted from the composite mass to find the epoxy mass of each composite specimen. Values for densities of cured epoxy mixtures and carbon fibers permitted calculation of fiber volume fraction.

Samples to be used to check for internal stress by sample radius of curvature consisted of a 0/90 bilayer. Samples to be used for mechanical tests were unidirectional. Samples sent to Dan Post at Virginia Polytechnic Institute for internal stress measurement by an interferometric method were 0/(90)₂/0. Samples were also sent to Larry Drzal for nanoindentation testing.

Dynamic mechanical thermal analysis was performed on a Polymer Laboratories Instrument by Mr. Timothy Dapp of the Polymer Composites and Resins Branch, DTRC, and differential scanning calorimetry was done by Mr. George Long of the Fire Protection and Survival Branch on a DuPont 9900 Thermal Analyzer. Mechanical tests of the graphite fiber reinforced composites were done on a Universal Test Machine.

Results and Discussion

Differential scanning calorimetry traces (Fig. 1) provide information about the extent of cure which has taken place. From these it may be seen that curing for the DNSOC - epoxy was considerably slower than for the epoxy only. Amount of shrinkage or expansion which occurred with various compositions and curing conditions are shown in Table 1. For the 5% DNSOC sample cured for 24 hours at 150 °C there was almost no shrinkage.

Tensile property measurements made on the neat resin with and without 5% DNSOC appear in Table 2. Tensile modulus is not much affected by DNSOC incorporation, but tensile strength is higher for the unreinforced DNSOC containing resin than for the epoxy control.

Mechanical property test results for the composite samples appear in Table 3. Samples tested consisted of 10 layers layed up so as to be unidirectional. Tests performed were compression, short beam shear and flexure. The fiber volume fractions were significantly greater for the epoxy than for the DNSOC - epoxy because the viscosity of the epoxy mixture containing DNSOC was larger than that of the epoxy only. If measured values for mechanical properties are adjusted for differences in fiber volume fraction, the mechanical properties are superior for the DNSOC - epoxy samples as seen in Table 4. However, the adjusted value was not actually measured at DTRC.

When measurements of fiber volume fraction are made, it is possible to use the data to calculate void volume for the samples. It is of interest to note that for the epoxy graphite

fiber sample the void volume was found to be 5.4%, but for the comparable DNSOC containing sample the void volume was zero (within the experimental error of the measurements. When all five of the data points were used, the void volume was calculated to be -0.077%; use of the four data points having values closest, yielded the value 0.0083%. The ASTM procedure calls for measurements of five values). Reduction in void volume could reasonably be expected to decrease the sample moisture sensitivity as was observed by Dr. Piggott for DNSOC containing carbon fiber reinforced samples relative to epoxy carbon samples.

Dynamic mechanical thermal analysis results are shown in Figs. 2 and 3. When the curing was done at 100 °C for four hours, 2 hours at 150 °C, and seven hours at 180 °C, the T_g is 100 °C for the epoxy control but is reduced by about 10 °C for the 11.7% DNSOC - epoxy as shown in Fig. 2. When the cure cycle was 100 °C for four hours followed by 150 °C for 24 hours, the epoxy showed two T_g peak, one at 100 °C and one at 150 °C. However, these were greatly reduced in magnitude from those seen on samples cured for shorter periods, indicating that extensive crosslinking has occurred. The 5% DNSOC - epoxy showed a single T_g at 100 °C. (Fig. 3), a value comparable to that seen for epoxy cured as in Fig. 2. It can be concluded from these results that a longer time is required to cure the system when it contains DNSOC.

Several methods were utilized to get information about the residual stress of the cured composite resin. A qualitative assessment was made by viewing the resin with an embedded single filament under a microscope through crossed polarizers. The resulting micrograph is shown in Fig. 4. Fiber waviness seen in the photo of the epoxy containing a single graphite fiber indicates longitudinal compressive stress on the fiber. Colored areas were also observed in the epoxy which indicate residual strain in the matrix. Cure for this sample was done at 150 °C. Photos of the DNSOC-epoxy matrices containing a single fiber lacked the colored regions and fiber waviness was not observed.

The second method used to measure residual stress was done by preparing 0/90 bilayer carbon fiber reinforced sample. The curvature of the six inch square composite sample, cured at 150°C for 24 hours, with and without 5% DNSOC, is shown in Fig. 5. The presence of DNSOC reduces the curvature by approximately a factor of two. However, the 9% greater fiber volume fraction in the epoxy sample contributes to an unknown extent to an increase in strain in this sample.

Results of the embedded single filament test which is performed on small dogbone specimens with $1 \times 4 \text{ mm}^2$ cross sections, showed that for the epoxy matrix the fiber pieces were approximately 1 mm, yielding a value of 19.7 MPa for the interfacial shear strength (IFSS), but for the matrix containing 11.7% DNSOC the pieces were much longer (Very approximately, one

cm.)). The values found with the nanoindentation test, for which portions are cut from 6"x6" specimens containing approximately 60% carbon fibers, for the IFSS in the laboratory of Lawrence Drzal for carbon fiber reinforced epoxy composites with and without 5% DNSOC are shown in Table 5. They indicate that IFSS has been reduced approximately 33% by the DNSOC, to 50 MPa.

Residual stress was measured for 5 x 5 inch [0/90₂/0]_T carbon fiber reinforced epoxy samples with and without 5% DNSOC. Because the uncured epoxy mixture containing 5% DNSOC has a higher viscosity than the epoxy without it, more matrix coated the fibers during the prepregging process. The result was that each epoxy layer was 0.025 inch thick and each 5% DNSOC layer was 0.035 inch thick and the DNSOC-epoxy had a lower fiber volume fraction as reported in Table 1. When interferometric measurements were made, it was found possible to compensate for the differences in layer thickness, but the difference in fiber volume fraction is an unresolved problem because the smaller fiber volume fraction in the DNSOC - epoxy sample contributes to reduced residual strain. With these differences in mind, the 5% DNSOC sample was found to have smaller residual strains perpendicular to the plies by about 20 %. However, further interpretation of DNSOC effect is not possible. Test results are shown in figures 6, 7 and 8.

It can be argued that each of the residual strain measurements is in some way flawed and therefore may not be totally reliable. However, all the tests point in the same direction; namely that residual strain is reduced by inclusion of a rather small amount of DNSOC, while the mechanical properties measured are comparable for the two sets of samples.

The results obtained on the David Taylor samples are in striking contrast to those obtained by Dan Post on samples prepared in the laboratory of Prof. Anthony Vizzini (1990) at the University of Maryland. These carbon fiber reinforced samples contained 20% DNSOC, but were found to have no reduction in internal stress as compared with control epoxy samples. This result can be explained by the fact that if DNSOC is to be effective in controlling shrinkage, and hence residual strain, it is first of all necessary to employ a dispersion of the DNSOC which has most of the particles below 10 μm in size. Secondly, it is necessary to use a dual catalyst system which first causes the epoxy to gel, then triggers the DNSOC reaction which occurs at a higher temperature. These things were not done.

No time versus product studies have been made to actually monitor the course of this reaction with the system employed at DTRC. However, it has been observed by us that the epoxy mixture containing the DNSOC requires a longer heating period for cure, 24 hours at 150 °C, than the epoxy only which will cure satisfactorily in 4 hours at 150 °C. For our work the mPDA was used as the curing agent for the epoxy, and the BF₃ triggered

reaction of the DNSOC.

An interesting result was obtained when 5% DNSOC - epoxy samples were being molded. The adhered so tightly to the mold surface, even when it was teflon coated or sprayed with silicone mold release agent, that the sample could not be removed from the metal mold without breaking it unless it was reheated.

Conclusions

Incorporation of DNSOC in amounts as small as 5% can effectively control epoxy composite shrinkage. T_g is not lowered by DNSOC incorporation, and mechanical properties appear better for DNSOC - epoxy controls than for epoxy composites if fiber volume fraction is taken into account. All tests performed to measure residual strain; microscopy, 0/90 layup, and interferometry indicate strain reduction. However, the larger fiber volume fraction in the epoxy samples plays a role in strain reduction in the 0/90 layup and interferometry samples. Interfacial shear stress reductions, seen by the embedded single filament and nanoindentation tests, are not affected by the fiber volume difference. The shrinkage control provided by DNSOC has a large, unexplored potential for relieving stress in thick section composites, and waviness in filament wound cylinders.

The nonshrinking epoxy matrix can also be used in precision molding. Epoxy containing expanding monomer attaches tenaciously to low energy surfaces.

TABLE 1
VOLUME EFFECT OF INCORPORATING DNSOC

| Substance | Curing Agents | Highest Cure Temp °C | Volume Reduction |
|------------------------|---------------|-------------------------|---------------------|
| Epoxy (Epon 813) | mPDA | 180 | 5.4 |
| Epoxy-DNSOC (11.7%) | mPDA | 180 | 0% |
| Epoxy (Epon 815) | mPDA | 150 | 3.1% |
| Epoxy-DNSOC (5%) | mPDA | 150 | 0.003% |

TABLE 2
TENSILE PROPERTIES OF THE NEAT RESIN

| Sample | n | Tensile Modulus MSI \pm SD, (GPa) | Tensile Strength KSI \pm SD (MPa) |
|---------------------|---|---|---|
| Epoxy 815 | 6 | 0.425 \pm 0.058 (2.93 \pm 0.40) | 4.64 \pm 0.88 (31.9 \pm 6.1) |
| Epoxy-DNSOC (5%) | 2 | 0.494 \pm 0.0912 (3.40 \pm 0.63) | 6.76 \pm 0.141 (46.6 \pm 0.97) |

Table 3
MECHANICAL PROPERTIES
Carbon Fiber Composites

| Test | Epoxy FVF 67.9% (SD $\pm 1.5\%$) KSI \pm SD (MPa \pm SD) | n | 5% DNSOC-epoxy FVF 58.6% (SD $\pm 1.8\%$) KSI \pm SD (MPa \pm SD) | n |
|------------------|---|---|--|---|
| Compression | 111 \pm 14 (755 \pm 96) | 5 | 108 \pm 96 (744 \pm 150) | 7 |
| Short beam shear | 10.9 \pm 0.19 (75 \pm 1.3) | 5 | 9.7 \pm 0.61 (67 \pm 4.2) | 5 |
| Flexure | 184 \pm 14 (1270 \pm 96) | 6 | 176 \pm 12 (1210 \pm 83) | 8 |

Table 4
MECHANICAL PROPERTIES
(Corrected to 60% carbon fiber volume fraction)

| Test | Epoxy KSI (MPa) | 5% DNSOC-epoxy KSI (MPa) |
|--------------|-----------------------|--------------------------------|
| Compresssion | 89 (613) | 110 (758) |
| Flexure | 163 (1120) | 180 (1240) |

TABLE 5
NANOINDENTATION RESULTS*

| Sample | IFSS, psi (MPa) | S.D., psi (MPa) | n |
|--------------------------|--------------------|--------------------|----|
| Neat epoxy (Epon 815) | 10800 (73.4) | 1000 (6.9) | 10 |
| Epoxy/5%DNSOC | 7200 (49.6) | 800 (5.5) | 10 |

*Performed in the laboratory of Dr. Lawrence Drzal at Michigan State University.

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The help of Dr. Lawrence Drzal in performing the nanoindentation test, and of Dr. Daniel Post in doing the interferometric strain measurements is very much appreciated.

Assistance from Mr. Timothy Dapp and Mr. George Long is also acknowledged and appreciated.

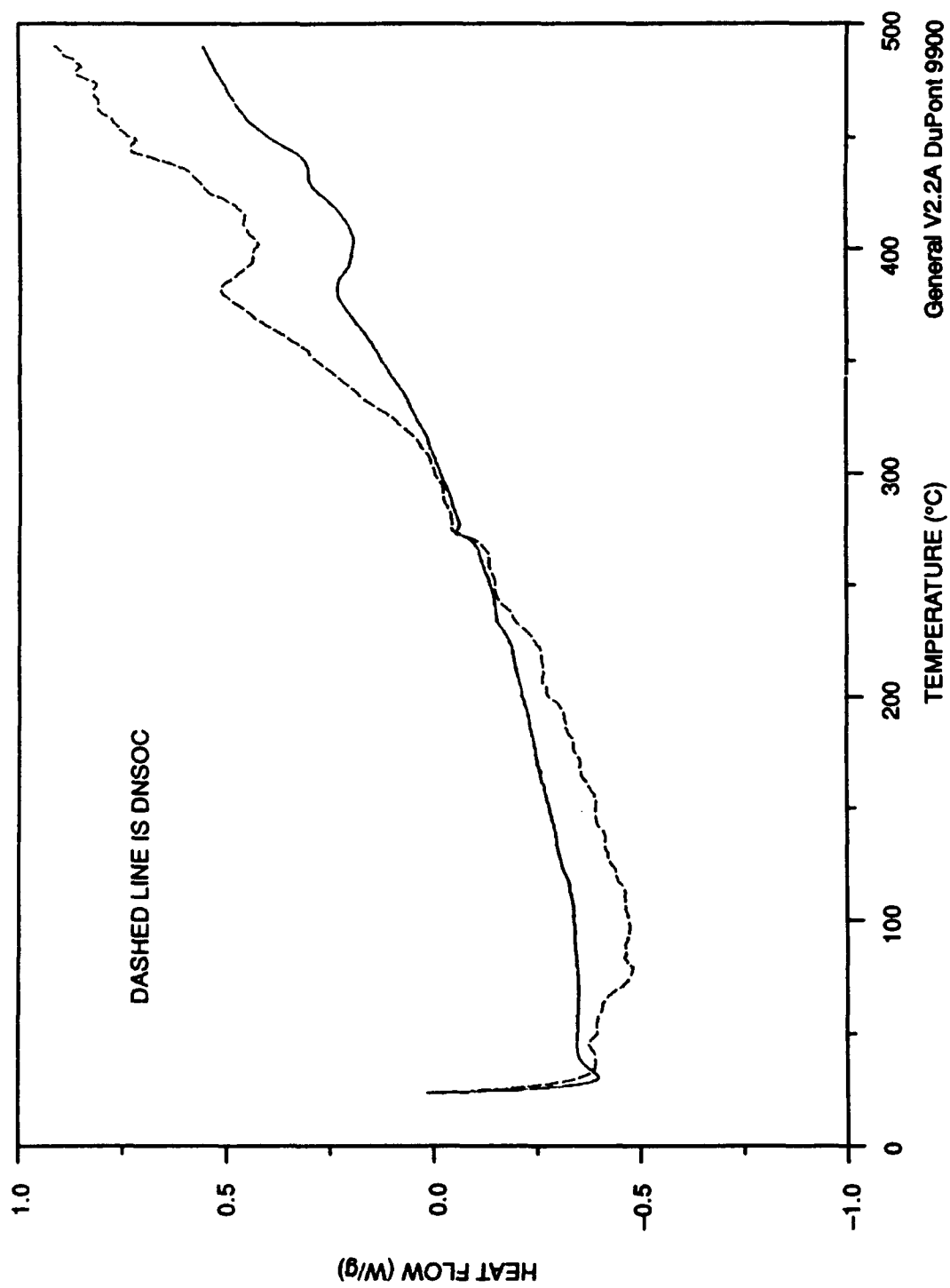


Fig. 1 Differential scanning calorimetry results.

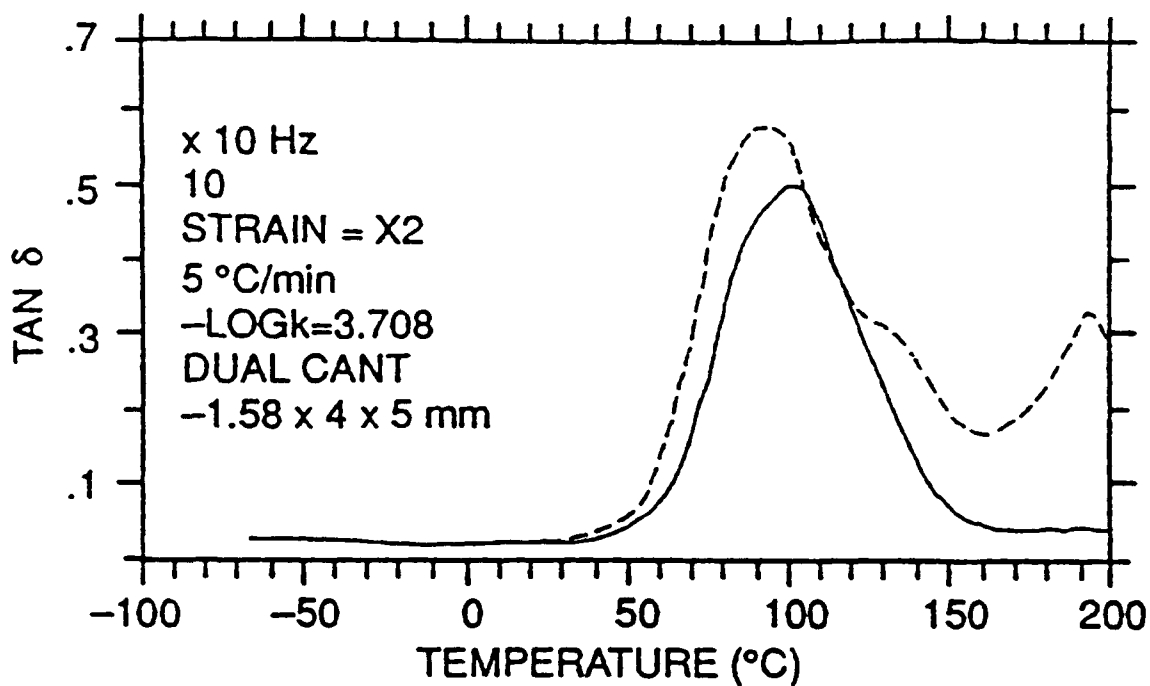


Fig. 2. Dynamic mechanical thermal analysis results for Epon 813 epoxy and for Epon 813 containing 11.7% DNSOC. The DNSOC-containing sample had a lower T_g by about 10°C, 2 hours at 150°C, and 7 hours at 180°C.

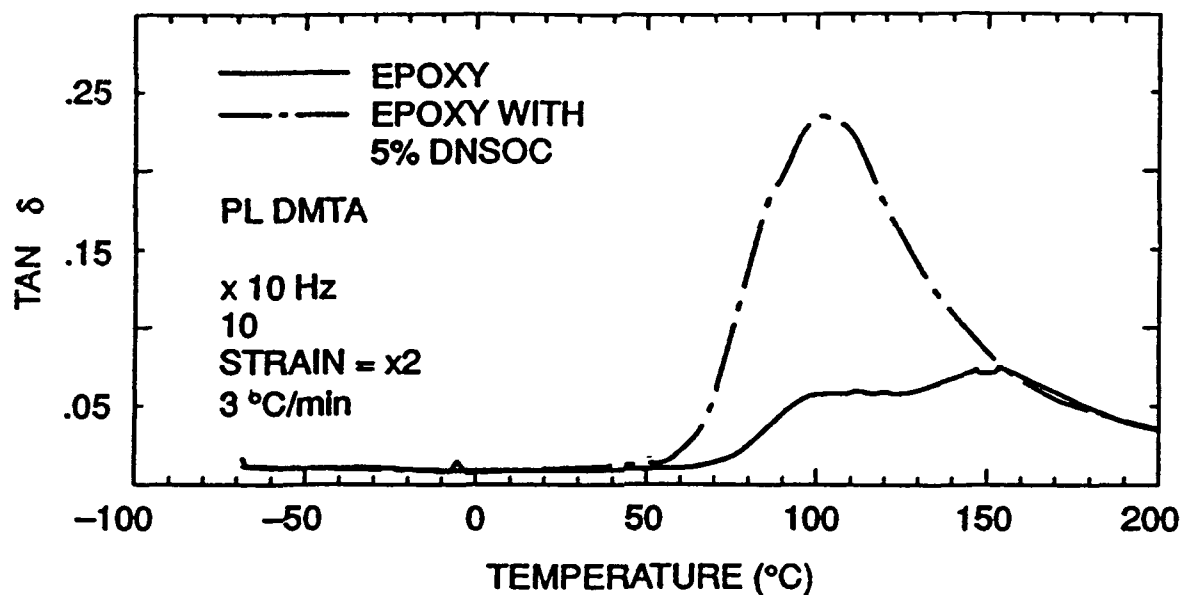


Fig. 3. Dynamic mechanical thermal analysis results for Epon 815 epoxy and for Epon 815 containing 5% DNSOC cured for 4 hours in an autoclave at 100°C followed by 24 hours at 150°C. Because of the increased crosslinking caused by the longer heating time, much of the epoxy T_g indication has been lost.

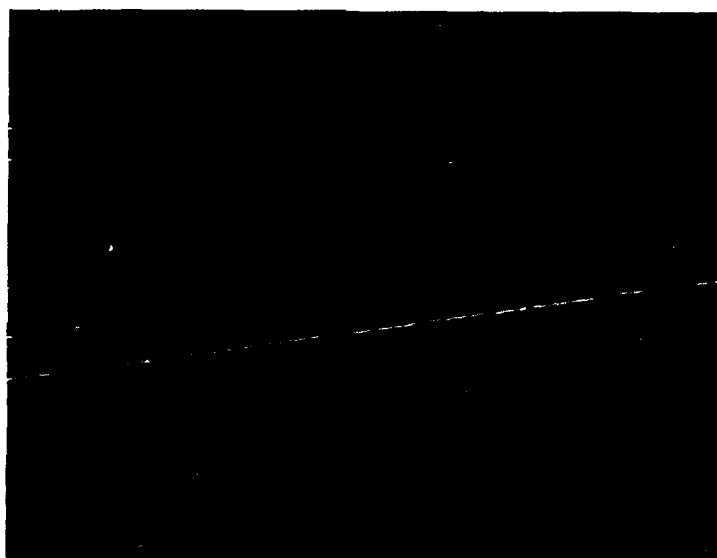


Fig. 4. Micrograph taken with crossed polarizers for Epon 813 epoxy cured at 150°C for 4 hours. Fiber waviness and colored areas indicate matrix stress.

STRAIN MEASURED FROM RADIUS OF CURVATURE

| SAMPLE | L (cm) | C (cm) | R (cm) |
|-----------------|--------|--------|--------|
| EPOXY (E) | 0.8 | 14.2 | 31.9 |
| 5% DNSOC-EP (D) | 0.4 | 14.5 | 65.9 |

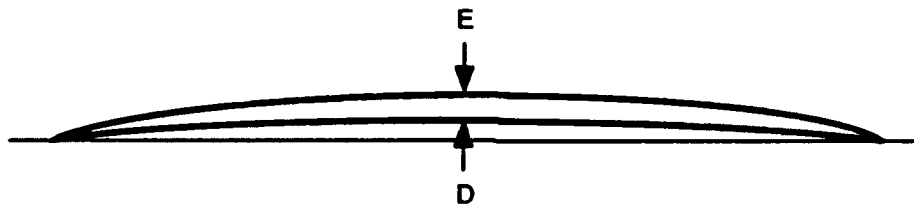


Fig. 5. Curvature of 6 x 6 inch 0/90 composite squares, cured at 100 °C for 4 hours and at 150 °C for 24 hours in an autoclave.

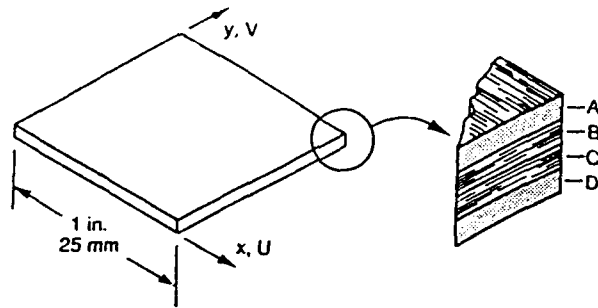


Fig. 6a.

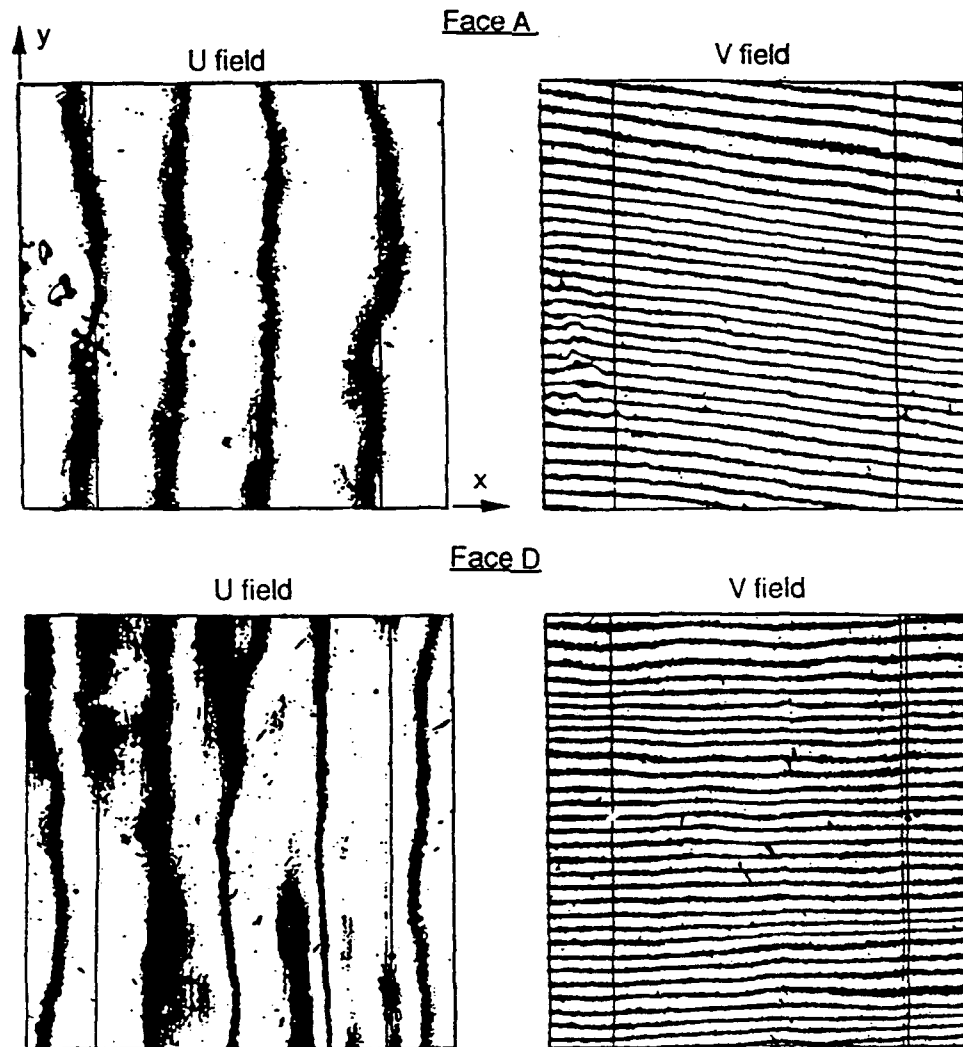


Fig. 6b. Experimental (Non-shrink Matrix).

Fig. 6. Interferogram stress measurement for faces A and D of the 5% DNSOC-epoxy sample.

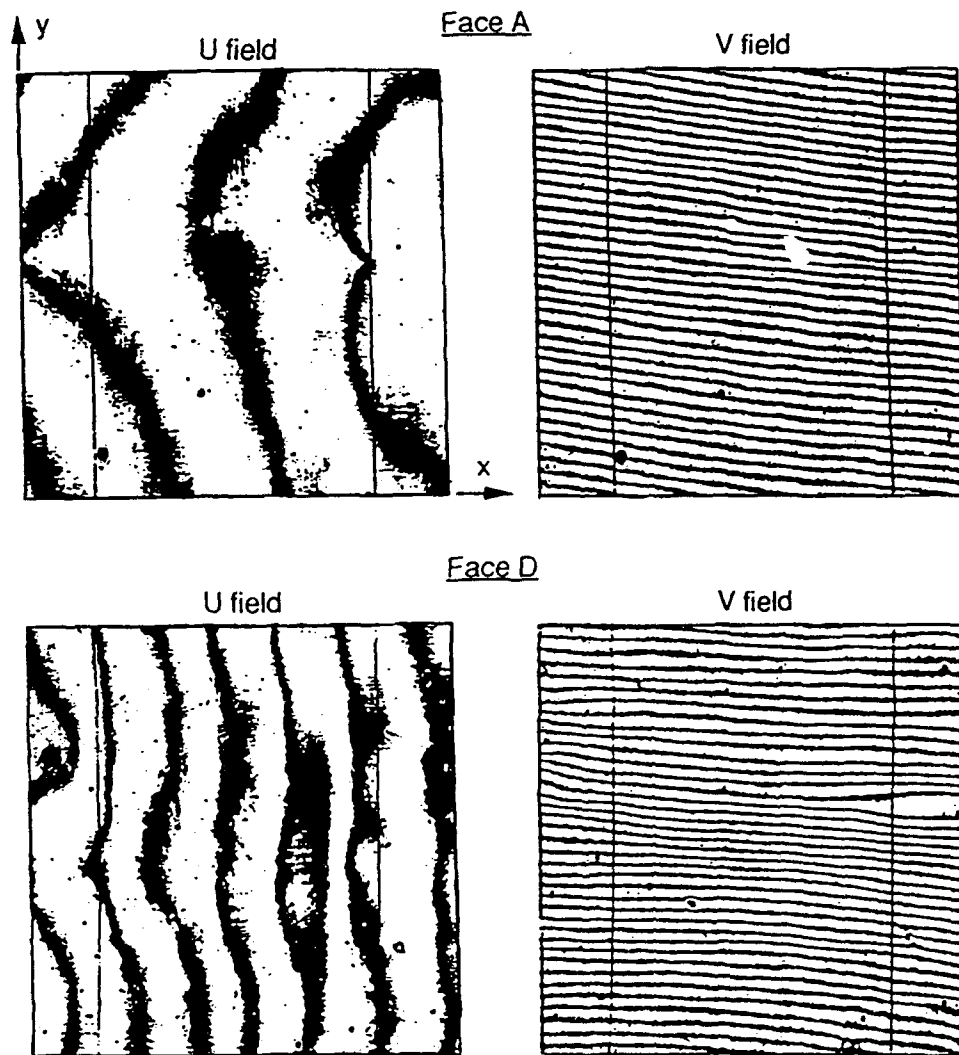
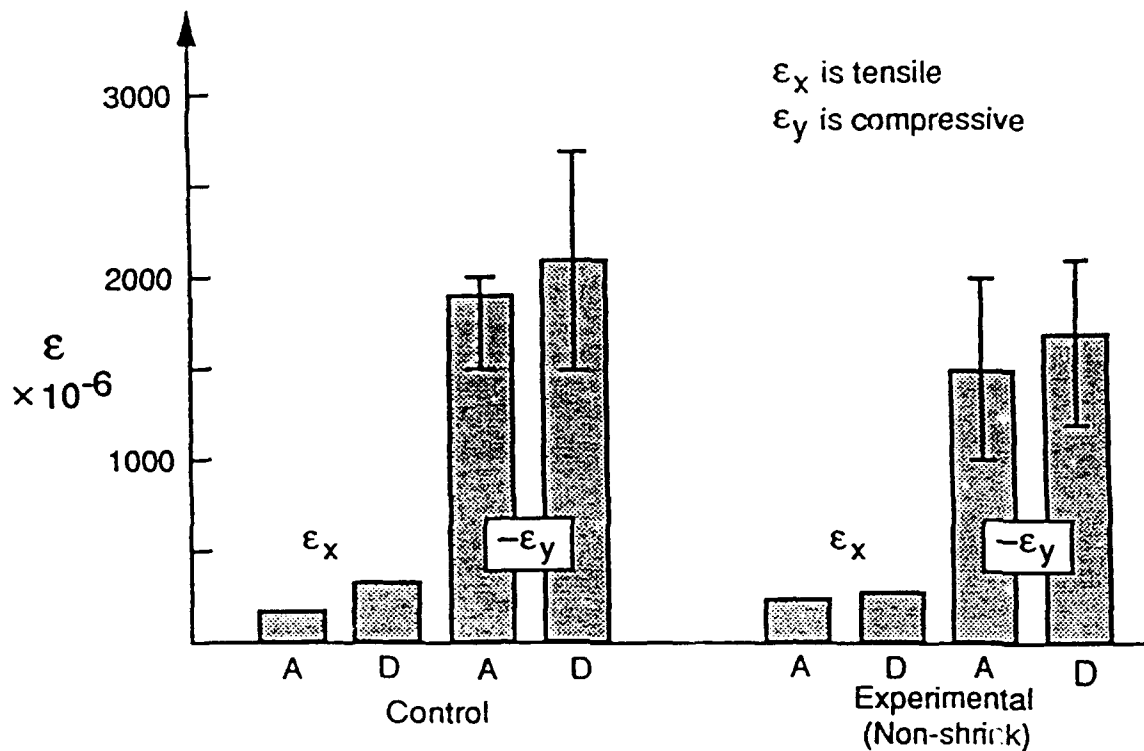


Fig. 7. Epoxy control interferogram stress measurement results for faces A and D. Measurements made on sample portion as shown in Fig. 6a.



| | | | $\epsilon_x (\mu\epsilon)$ | $\epsilon_y (\mu\epsilon)$ |
|-------------------------------------|--------|------|----------------------------|----------------------------|
| Experimental (Non-shrink Matrix) | Face A | high | 240 | -2000 |
| | | avg | | -1500 |
| | | low | | -1000 |
| | Face D | high | 260 | -2100 |
| | | avg | | -1700 |
| | | low | | -1200 |
| Control | Face A | high | 170 | -2000 |
| | | avg | | -1900 |
| | | low | | -1500 |
| | Face D | high | 320 | -2700 |
| | | avg | | -2100 |
| | | low | | -1500 |

Fig. 8. Plot of interferogram test results showing that residual compressive stress is lowered by 20% for the 5% DNSOC-epoxy. Values are comparable for residual tensile stress for the 5% DNSOC sample and the control.

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| 13. ABSTRACT (Maximum 200 words) <p>In this investigation it was confirmed that copolymerization of dinorbornene spiroorthocarbonate (DNSOC) with epoxy can eliminate sample shrinkage and even produce sample expansion. To maximize control of shrinkage, it is important to bring epoxy to the gel stage before the DNSOC begins to copolymerize.</p> <p>DGEBA epoxy was cured with m-phenylenediamine (mPDA) and DNSOC-epoxy samples were cured with mPDA and BF₃.diethylenetriamine (BF₃ was used to catalyze polymerization of the DNSOC). As compared with carbon fiber reinforced epoxy, the sample with 5% DNSOC showed 33% reduction in interfacial shear stress as measured by the nanoindentation test, and reduction in residual stress perpendicular to the plies by interferometry. However, the significant differences in fiber volume fraction between the epoxy samples can account for some of this apparent reduction. The resin itself showed increases in both tensile strength and tensile modulus when 5% DNSOC was incorporated, and the sample showed no shrinkage.</p> | | | | |
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